

Operando X-ray absorption and emission spectroscopic study of V-W-TiO₂ catalysts for NO_x removal from the diesel exhaust

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A large number of heavy-duty diesel engines worldwide are equipped with vanadia-based catalysts for Selective Catalytic Reduction of NO_x with NH₃ (NH₃-SCR). X-ray absorption spectroscopy (XAS) is a technique of choice for understanding changes in the oxidation state and coordination environment of active sites during real catalyst operation, i.e. *operando* [1]. V K edge X-ray absorption near edge structure (XANES) region is very sensitive to its oxidation state and coordination environment which makes it attractive also for catalysis research. However, so far *in situ* or *operando* studies on the realistic V-W/TiO₂ system have not been reported. The reason is a combination of highly absorbing W-containing support nearly prohibiting transmission XAS and abundant Ti Kβ_{1,3} lines of which overlap with V Kα_{1,2}, thus, prohibiting conventional fluorescence measurements. Using X-ray emission spectrometers based on crystal analyzers allows resolving Ti and V fluorescence lines and record high energy resolution fluorescence detected (HERFD)-XAS data on the realistic V-W/TiO₂ under working conditions.

A series of V-W/TiO₂ and V/TiO₂ catalysts with highly dispersed isolated and polymeric V oxo-species and high activity towards NH₃-SCR were synthesized by incipient wetness impregnation and grafting [2]. HERFD-XANES and XES measurements were carried out at ID26 beamline of the European Synchrotron Radiation Facility using a Johann-type emission spectrometer equipped with four spherically bent Ge (422) analyzer crystals. For collecting *operando* spectra a setup with a heated quartz capillary microreactor (plug flow geometry, diameter 1 mm, wall thickness 0.01 mm, heated with an air blower) was used, typical conditions were 1000 ppm NO or 1000 ppm NO₂, 1000 ppm NH₃, 5% O₂, 0-1.5% H₂O in He at 250 or 400 °C. Outlet gas analysis was performed using an MKS MultiGas 2030 FTIR.

Variations in the Kβ_{1,3} XES and the pre-edge region of HERFD-XANES indicate redox switching of V sites between V⁴⁺ and V⁵⁺ states during NH₃-SCR and under related model conditions. In contrast, the shape of V-K XANES spectra is very sensitive to variations in the coordination geometry, however, no significant changes in the HERFD-XANES were observed revealing an almost unchanged geometry of V sites. The formation of a direct V-N bond was not observed in the valence-to-core region of the X-ray emission spectra compared to our earlier results in Cu- and Fe-based zeolites [3]. However, the slight changes of the vtc-XES region observed at low but also high temperatures, particularly in the presence of pure NH₃ and of NO+O₂, clearly suggest the adsorption of these species most probably via a neighboring O atom or at interfacial sites with the TiO₂ or WO₃/TiO₂ support.

The obtained information indicates that the role of V species in NH₃-SCR is to provide redox sites and also to facilitate the interaction between NH₃ and NO. The results of this first *operando* XAS/XES study of V-W/TiO₂ catalysts allow better understanding the SCR mechanism which may lead to improved catalyst design and better kinetic models.

References:

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